A STUDY ON THE DISTRIBUTION OF VARIOUS CHEMICAL SPECIES IN DIFFERENT COAL LIQUIDS BY SIZE EXCLUSION CHROMATOGRAPHY - GAS CHROMATOGRAPHY - MASS SPECTROMETRY

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INTRODUCTION

Size exclusion chromatography - gas chromatography - mass spectrometry (SEC-GC-MS) is a unique technique which we have developed for coal liquid analysis. Size exclusion chromatography (SEC) separates molecules based on size in a short analysis time. Unlike other chromatographic techniques, SEC does not retain sample species on the column, the analysis time is fixed, and everything loaded onto the column elutes within a fixed time frame. The application of SEC is limited only by the solubility of the sample in a solvent. Since tetrahydrofuran (THF) is a good solvent for coal liquids, the separation of coal liquids by SEC is easily achieved with appropriate columns. Although size exclusion chromatography (SEC) has been used primarily for the separation and characterization of polymers based on molecular size or molecular weight, its use can be extended to the separation of smaller size molecules (1-4). Since coal-derived mixtures have several components of similar sizes, the use of SEC alone does not resolve them for the purpose of identification.

Coal liquids, petroleum crudes, and their distillation cuts have been separated into four or five fractions by SEC. These SEC fractions were analyzed by use of GC (6,7,8). The fraction collection procedure was performed manually, which was inefficient, and susceptible to human error (9,10,11,12,13). A preferred technique is to use a computer controlled fraction collection and subsequent GC-MS analysis technique (14,15,16,17,18). The automated fraction collection followed by injection of the fraction into the GC reduces analysis time, and offers an option for the collection of the desired number of fractions at predetermined time intervals. The manual collection of up to 10 one-ml fractions is also used in order to varify the effectiveness of the automated technique.

Mass spectrometers used to be expensive and complex for routine use as a GC detector. The Ion Trap Detector (ITD, Finnigan) is a low priced mass spectrometer (MS) for capillary chromatography. Three analytical tools - SEC, GC, and ITD - are incorporated into a powerful analytical system for the analysis of complex mixtures such as coal liquids, recyle solvent and anthracene oils. The SEC-GC-MS analysis of Wyodak recycle solvent is used to illustrate the speed and effectiveness of the technique.

EXPERIMENTAL

The low rank coals used in the liquefaction experiments were Texas Big Brown lignite from the Wilcox formation, Zap-2 Indian Head lignite and Beulah lignite from North Dakota and Wyodak coal from Wyoming. Mini reactors (6.3 and 20 mℓ) used mostly Autoclave high pressure fittings (11). The liquefaction solvents included anthracene oil, four recycle solvents from the coal liquefaction pilot plant at the University of North Dakota Energy Research Center (UNDERC) and water under supercritical conditions. Hydrogen, carbon monoxide and hydrogen sulphide were the reactive gases which were used in varying proportions (19). The samples of liquid products from selected experimental conditions were used for the detailed analysis.

The product slurry as well as the recycle solvents were extracted with tetrahydrofuran (THF) and the solubles were used as samples for the analysis. The technique for the analysis is based on the integrated use of three instruments - a size exclusion chromatograph (SEC) with a 100Å SEC column, a high resolution gas chromatograph with a bonded phase wide bore fused silica column and an Ion Trap Detector (ITD, Finnigan), a mass spectrometer for capillary chromatograph (Figure 1). A sample injected into the SEC was separated based on linear molecular size and the fractions of effluents were collected at preprogramed time intervals. The SEC-GC interface is illustrated in Figure 2. The separation of each fraction is continued on the capillary column and the components were detected by the mass spectrometer (ITD). The mass spectral fragmentation data were stored on a 10 megabyte hard disk and were later analyzed by the library search using National Bureau of Standards (NBS) mass spectral data base which has fragmentation patterns of about 40,000 organic compounds. The library search was used to identify the general formula as well as probable functional groups of most major components in coal liquids. The identification of each species was achieved by using several factors including SEC retention volume (linear molecular size), GC retention time (boiling point, molecular weight) and mass spectral fragmentation pattern. Since the coal liquids contain many components, the mass spectral data of some compounds were not available in the library. A very careful evaluation of the MS fragmentation pattern was necessary to establish the identity of the compound. Identification of unknowns needed better MS fragmentation pattern and time. Once a compound was identified, the information was continously used for identifying trace amounts based on masses of the major fragments.

RESULTS & DISCUSSION

Analysis of Wyodak recycle solvent

The detailed discussion of SEC-GC-MS analysis Wyodak recycle solvent can be used to illustrate the analysis technique as well as the composition of coal liquids. Wyodak recycle solvent contains some anthracene oil distillate as well as coal depolymonization products stabilized by the liquefaction conditions. Figure 3 shows the SEC separation of Wyodak recycle solvent. The separation pattern of various chemical species and chemical groups are assigned based on reported (4-15) as well as unreported studies. When valves V_2 and V_3 (Figure 2) are engaged, the SEC effluents are collected in the sample loops of V_3 at specific intervals. The refractive index detector output shows the effect of such fraction collections as negative peaks (Figure 4). Sixteen SEC fractions of 100 μl each were collected from the Wyodak recycle solvent (Figure 4) at 0.5 min intervals. Each fraction was analyzed by injecting 0.1 μl into the GC, which used the flame ionization detector (FID). The first three fractions and the last fraction showed the GC of the solvent; so the GC of those fractions are not included in Figure 5. The first GC (Figure 5.1) corresponds to the GC of fraction #4 and the last GC (Figure 5.12) is that of fraction #15. By increasing the GC oven temperature the larger alkanes in fraction #2 and #3 can be detected. A shorter column enhances the FID response as these heavy alkanes accumulate on the column probably due to irreversible adsorption or decomposition.

Figure 5.1 shows the GC of fraction #4. It shows alkanes ranging from C_{25} to C_{30}. It is quite possible that the fraction may contain higher alkanes which are not detected due to the GC-oven temperature limit. The peaks are identified from the MS fragmentation pattern. Fraction #5 is collected after a 0.5 minute interval and its GC (Figure 5.2) shows alkanes ranging from C_{19} to C_{30}. This fraction has lower alkanes (C_{19}-C_{24}) in larger proportions in addition to smaller amounts of alkanes

(C_{25}-C_{30}) which were detected earlier in fraction #4. The peak due to C_{27} is larger relatively to other alkanes in Figure 5.1 and 5.2. Our experience with fossil fuels indicates that the straight chain alkanes (n-alkanes) have a normal distribution over a wide molecular weight range. Even in other reported works on hydrocarbon fuels an unusual enhancement of a particular straight chain alkane is not observed. The alkane fractions always contain branched alkanes such as pristane, phytane, and hopane, and some of them are called biological markers. It is quite possible that the C_{27} peak could be due to some branched alkanes co-eluting with n-C_{27}.

The GC of fraction #6 is shown in Figure 5.3, which contains mostly alkanes in the range of C_{15}-C_{24} and small amounts of C_{14} and C_{25}-C_{29}. The fraction #6 was collected 0.5 minute after fraction #5 and one minute after fraction #4. If fraction #5 had not been collected, the GC of fraction #4 and #6 which were one minute apart could have been used to qualitatively, but not necessarily qualitatively, determine all of the species. Fraction #5 has species from both fractions #4 and #6. The peak width of species eluting at these retention times is about one minute. Hence SEC fraction collection at one min (one ml) intervals would have contained all the species with less overlapping and analysis time could have been reduced to half. A short peak immediately after C_{17} is pristane (trimethylhexadecane). The short peaks that appear between the n-alkane peaks appear to be isoalkanes or branched alkanes. The baseline appears to be shifted slightly upward compared to the baseline of the GC's in Figure 5.1 and 5.2. This is probably due to a large number of possible isomers of phenolic species. GC of fraction #7 (Figure 5.4) has alkanes as small as C_{12}. The ratio of peak heights of pristane to C_{17} increases in the GC of this fraction compared to previous fractions as expected from its shorter linear molecular size. The smaller peaks between n-alkane peaks are alkylated phenols and branched alkanes.

Fraction #8 (Figure 5.5) is mostly alkylated phenols and indanols with a trace amount of smaller alkanes. The baseline shift is due to the co-elution of several large phenolic species in many isomeric forms. Fraction #9 (Figure 5.6) does not contain any alkanes. The ratio of the o-cresols to m-, p-cresols increases from fraction #8 to #9. Both m-cresol and p-cresol are structurally longer than o-cresol. Some long aromatic species such as biphenyls also appear in this fraction. Compared to fraction #8, the phenols in fraction #9 are of shorter size while the peaks appearing at long GC retention times are aromatics. It is safe to say that phenols appear before 16 minutes of GC retention time followed by aromatics after 16 minutes. The GC of fraction #10 is shown in Figure 5.7. Light phenols including xylanols and cresols present in this fraction are separated on the GC before a retention time of 8 minutes. The species appearing after 8 minutes are aromatics, mostly with alkyl side chains.

Fraction #11, whose GC is in Figure 5.8, contains phenol, which appears at 3 minutes. Phenol is the only phenolic in Fraction 11. Almost all possible isomers of one and two ring aromatics with alkyl side chains (propyl or shorter) are detected in this fraction. Since the number of species are higher, co-elutions of two or more components at one GC retention time is observed. The mass spectral fragmentation pattern can be used to assign the molecular formula and general structural nature. The identification of isomers is very difficult in a number of cases. The NBS Mass Spectral Data Base has only a fraction of the needed standard reference spectra to identify the species in this fraction. Most of the identification has been assigned based on the fragmentation patterns and boiling points derived from the GC retention times. Fraction #12 as shown in Figure 5.9 has overlapping from two types of aromatics - alkylated aromatics and polycyclic aromatics. Fraction #13 contains aromatics with slight alkylation and the ring numbers increase as shown in Figure 5.10. Both fractions #14 and #15 (Figure 5.11, 5.12) contain only multi-ring aromatics with few alkyl side chains. One exception to the rule that SEC separates species in decreasing order of linear molecular size is that condensed ring aromatics tend to remain in the column longer. Some polycyclic aromatics such as pyrene and coronene are eluted from the gel column only after napthalene although they are much larger. More pyrene is in Fraction #15 than in Fraction #14 but the reverse is true for anthracene which appears before naphthalene.

Distribution of Alkanes in Coal Liquids

One of the major results of SEC-GC-MS studies is the discovery of an orderly pattern, by which various isomers and homologs of similar chemical species exist in coal liquids. For example almost any direct coal liquefaction process produces very similar species which differ from each other by size and extent of isomerization but with an orderly distribution pattern. Alkanes ranging from $C_{12}H_{26}$ and $C_{44}H_{80}$ are detected in almost any coal liquid. Most of these are straight chain alkanes showing an orderly continuous pattern. Neither is a particular n-alkane almost absent nor is it present in a disproportionate amount. Exceptions exist for some branched alkanes such as pristane, phytane, and hopane. These species are also called biomarkers and their concentration varies depending on the sample. The straight chain hydrocarbons, mainly the alkanes, are observed as sharp GC peaks in the GC of certain SEC fractions of lignite-derived liquids. The corresponding SEC-fractions of the anthracene oil show a "hump" in the GC. It appears that the pyrolytic conditions used in a coking oven are destroying or converting most of the straight-chain alkane species into numerous isomeric hydrocarbons. The MS fragmentation patterns of the GC "hump", are similar to that of alkanes.

Distribution of Phenols in Coal Liquids

Phenols are a major chemical lump present in coal liquids. Phenols have basically one or more aromatic ring structures with alkyl substituents. Methyl, ethyl and propyl are the most common alkyl substituents. The smallest species is the one with a hydroxyl group attached to a benzene ring. Addition of a methyl group produces three isomers - o-, m-, and p-cresols. It appears that all three are present in about the same proportion. The number of possible isomers increases as the possible number and size of alkyl substituents increases. It is expected that higher degree of alkylation can produce larger molecules in a larger number of isomeric forms, separation of which is rather difficult even by high resolution GC methods. This could be the reason why a shift in the GC baseline is observed for the SEC phenolic fractions rather than resolved peaks. Since these shifts are quite reproducible and real, it can be assumed that these "bumps" are due to a large number of components eluting continuously without resolution. Their SEC retention time suggests that they are probably phenols. The gas chromatographers who are used to fewer sharp peaks from capillary GC may prefer to resolve them. Sometimes derivatization techniques are used to obtain sharper well resolved peaks. As a matter of fact unresolved "bumps" are telling a story. Too many isomers of close molecular weight or boiling point are eluting without resolution at close retention times. Phenols do show peak tailing in most GC separation conditions. But currently available capillary columns do not show tailing as a serious problem. Peak tailing is expected to decrease as the degree of alkylation increases. Peak tailing for cresol is less than that for phenol. It is much improved for xylenols. The derivatization of phenols prior to GC separation may produce fewer well-resolved peaks but at the expense of losing some components.

Distribution of Aromatics in Coal Liquids

The number of isomers of alkylated aromatics is enormous. Lower members of alkylated benzenes such as xylenes are well-resolved and detected by FID and MS. Increased alkylation causes an increase in the number of isomers. In the case of both alkylated phenols and aromatics various isomers exist in a continuous pattern. The less alkylation gives few well-resolved isomers. The more alkylation gives a large number of isomers but in smaller concentrations.

We have observed a striking similarity in the identity of chemical species found in different types of coal liquids such as anthracene oil (AO4), recycle solvents and the lignite-derived liquids from our liquefaction experiments as they are separated by SEC-GC and identified by MS. The polycyclic aromatic species which are characteristic of coking oven products from coal, such as anthracene oil and creosote oil are found in all lignite-derived liquids from our liquefaction experiments, including the liquid obtained by the dissolution of lignite in water under super critical conditions. Their relative concentration was found to increase varying with the severity which is used to produce the coal liquid. Anthracene oil has the highest concentration of polycyclic aromatics and the lignite liquefied in supercritical water has the lowest. The hydroxy aromatics, also known as alkylated phenols, which are produced under lignite liquefaction experiments, are not major components in anthracene oil.

CONCLUSIONS

The coal conversion products are compounds of at least two types of species. "a" The species which are released from the coal matrix and stabilized by the coal liquefaction process. This type of species retains most of its original structural characteristics. Most of the alkanes and alkylated phenols belong to this group. "b" The species which are characteristic of high temperature reactions. The polycyclic aromatics such as phenanthrene and pyrenes are products of high temperature chemistry. Coke ovens and even wood burning fireplaces produce these products. The liquefaction environment can cause additions of alkyl side chains to these species although higher temperature causes the dealkylation of these products. Some of these species may be existing in coal but in lower concentrations.

The coal liquefaction process generates both types of compounds. Lower temperatures favor type "a" compounds while higher temperatures tend to produce more of type "b" compounds. The SEC-GC-MS analysis data on a number of coal liquids produced under varying conditions from different coals and liquefaction solvents indicate that liquefaction temperatures below 400°C produce very little type "b" compounds although they are not totally absent. The alkylated aromatics such as alkyl indans and benzenes appear to be generated from the original coal structure although these compounds could be catatytically generated at these temperatures even from simple starting materials such as CO and H_2. Several low temperature reactions products from coal support the existence of one or two ring aromatics with other substituents, especially in low rank coals.

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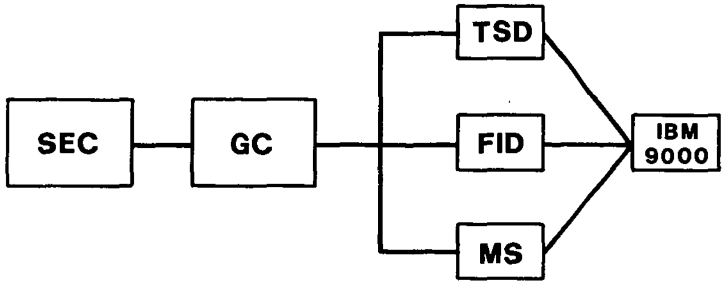

Figure 1. SEC-GC-MS instrumentation.

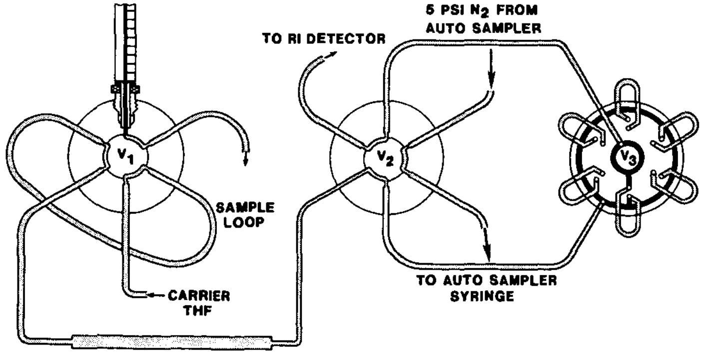

Figure 2. SEC-GC interface Note: V_3 has sixteen sample loops instead of six shown.

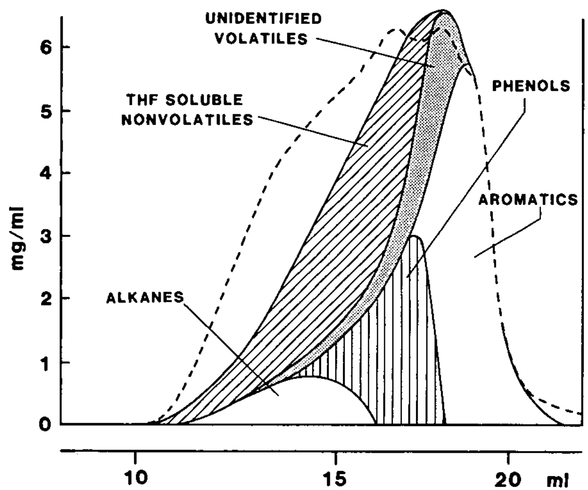

Figure 3. SEC of Wyodak recycle solvent.

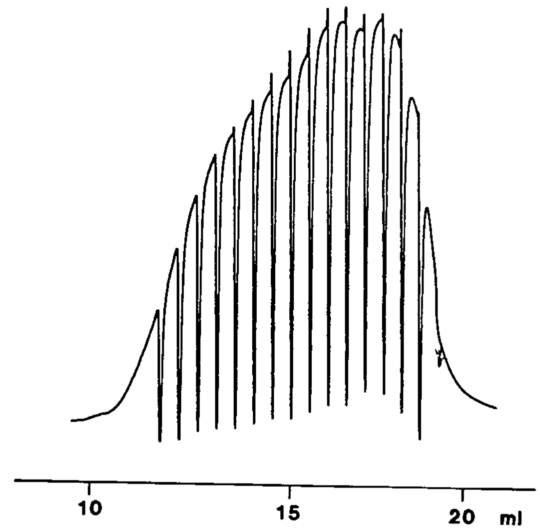

Figure 4. 100 µl fractions collected by SEC-GC interface (on-line).

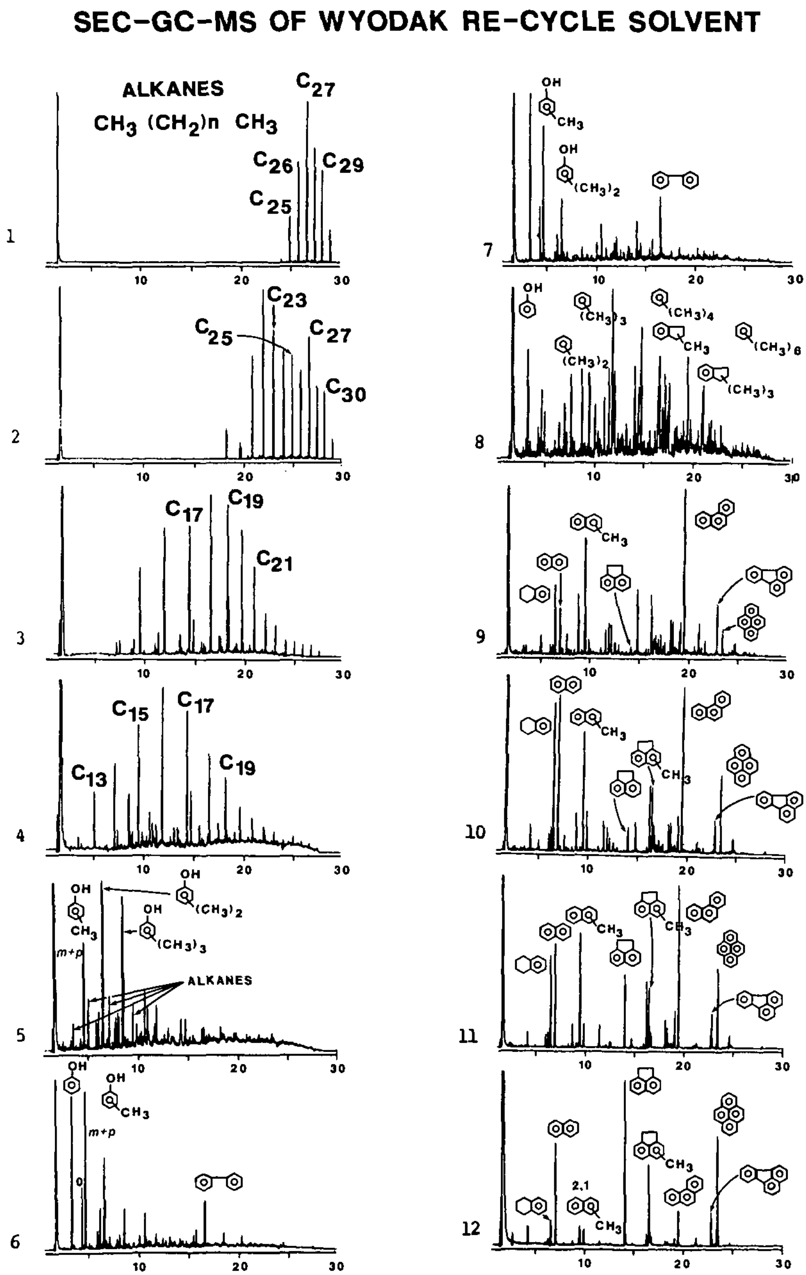

Figure 5. SEC-GC-MS of Wyodak re-cycle solvent.